

Electronically Modified Cobalt Aminopyridine Complexes Reveal an Orthogonal Axis for Catalytic Optimization for CO₂ Reduction

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Scientific Achievement

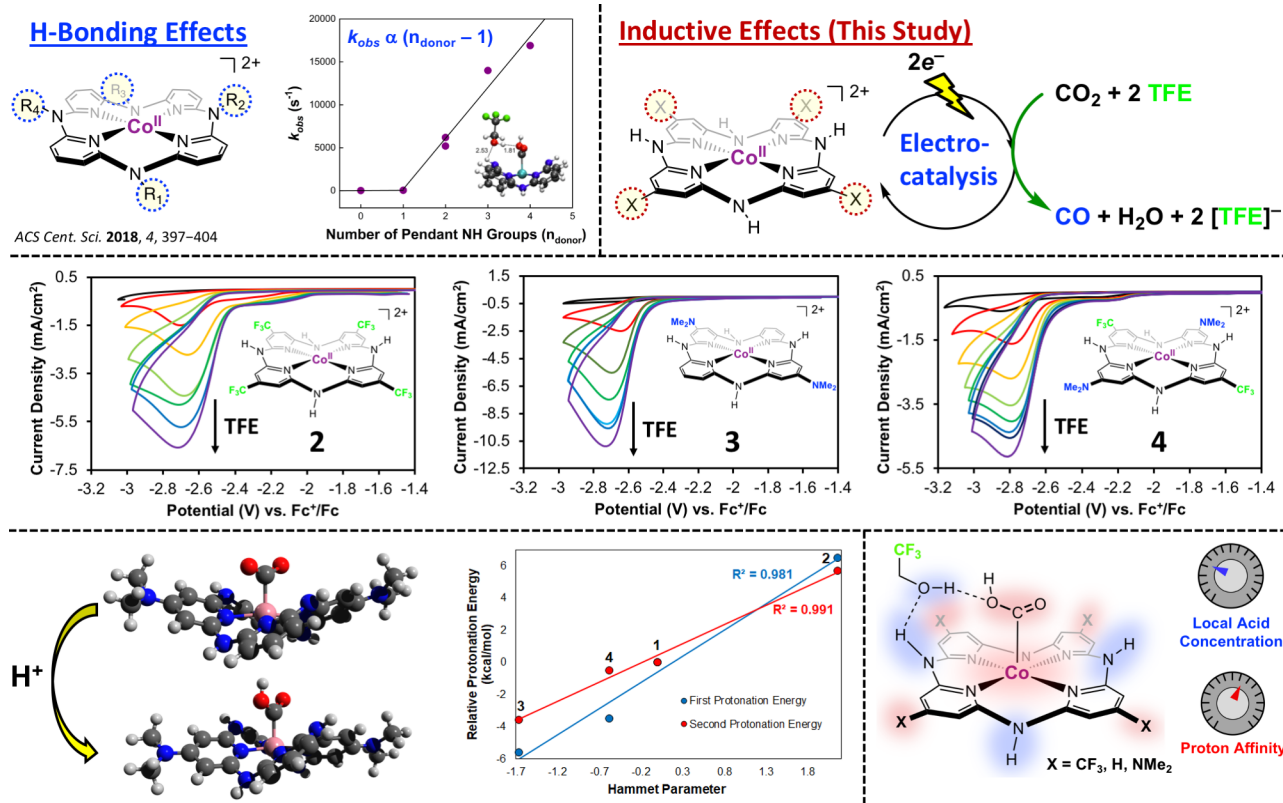
- We synthesized and investigated a family of molecular cobalt catalysts for electrochemical CO₂ reduction.

Significance and Impact

- Hydrogen-bonding and electronic inductive effects via chemical substitution can be utilized as orthogonal dials for catalytic tuning.

Technical Details

- Combined experimental and theoretical work finds electronic modification of the catalytic framework influences the basicity of critical Co-CO₂(H) intermediates.
- The most electrochemically active species via (i_{cat}/i_p) is predicted to have the most favorable Co-CO₂ proton binding energies.
- Hammett analysis is consistent with positive charge build up in the transition state ($r < 0$).



Incorporation of hydrogen bond donors into the framework of cobalt aminopyridine macrocycles has been demonstrated to increase the rate of reaction for electrochemical CO₂ reduction. Now further work has shown that electronic inductive effects imparted from chemical modification can influence catalysis through an orthogonal axis. Combined experimental and theoretical work suggests these inductive effects play a role in the basicity of critical reaction intermediates in the catalytic cycle.